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ANALYSIS OF NONVOLATILE RESIDUE (NVR) FROM SPACECRAFT SYSTEMS

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January 1985

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This document makes use of international metric units according to the Systeme International d'Unites (SI). In certain cases, utility requires the retention of other systems of units in addition to the SI units. The conventional units stated in parentheses following the computed SI equivalents are the basis of the measurements and calculations reported.

ABSTRACT

Organic contamination on critical spacecraft surfaces can cause electronic problems, serious attenuation of various optical signals, thermal control changes, and adhesion problems. Such contaminants can be detected early by the controlled use of witness mirrors, witness plates, wipe sampling, or direct solvent extraction. Each method requires careful control of variables of technique and materials to attain the ultimate sensitivities inherent to that procedure. Subsequent chemical analysis of the contaminant sample by infrared and mass spectrometry identifies the components, gives semiquantitative estimates of contaminant thickness, indicates possible sources of the nonvolatile residue (NVR), and provides guidance for effective cleanup procedures.

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INTRODUCTION

Nonvolatile residue (NVR) is the term that has evolved for the sum total of organic contaminants present on critical surfaces. Sometimes this term includes even inorganic oxides and particulates, although these substances will not be considered in the present treatment. In the terminology used here, the word "nonvolatile" implies only that the residue is not sufficiently volatile to be readily lost by evaporation under standard ambient conditions. Thus, NVR materials may become volatile under the influence of heat or reduced pressure, and detectable migration may occur under high-volume airflow (purge) or during long-term storage.

EFFECTS OF NVR

The effects of NVR on critical spacecraft components may range from minor annoyances to serious interference with the success of an entire experimental program. One of the more important effects of NVR is attenuation of optical signals in sensitive systems such as in telescope assemblies. The nature of this attenuation may be complex and may include optical absorption, scattering, diffraction, interference fringes, or combinations of these effects. NVR can cause electronic problems due to corrosion, changes in surface conductivity, and, in some high-voltage situations, can even lead to corona discharge. Many adhesion failures of potting compounds, coatings, adhesives, or paints have been traced to the presence of surface contaminants. Furthermore, it has been shown that many advanced electronic detector systems, ultrasensitive UV film detectors, and spark chamber assemblies are adversely influenced by NVR. In addition to these direct effects on hardware contaminated with NVR, the sensitivity of other components, which will be flown with and/or tested with that hardware, must be considered because NVR often becomes mobile in the vacuum environment and may be transferred to those adjacent critical surfaces.

DETECTION OF NVR

Detection of NVR occurs by any of several processes, the least desirable of which is the appearance of observable changes in system performance. Examples of these include loss of signal throughput in optical instruments, attenuation of detector responses, and chipping or peeling of paints or cracking

or loosening of potting materials. Sometimes NVR may be detected simply by visual observation. This is most likely with highly reflective surfaces viewed under strong lighting conditions. However, when the extreme sensitivity of a particular surface to small amounts of NVR dictates more controlled methods of detection, four relatively straightforward specific techniques are available. The more elegant and expensive direct surface analysis techniques such as electron spectroscopy for chemical analysis (ESCA) and secondary ion mass spectrometry (SIMS) are not considered here, since it has been found that the simpler and more practical methods suffice in most cases. The four techniques include the use of witness mirrors, witness plates, wipe samples, and direct solvent extraction, each followed by chemical analysis. The choice among these sampling techniques is usually determined by factors such as the ultimate sensitivity required, the specific property of the NVR that might be harmful, and practical matters such as system geometry and accessibility, and the skill and experience of technical personnel available to perform the task. Each of these techniques requires considerable pretest preparation, defined handling and sampling procedures, and proven expertise in analysis and measurement using that method.

WITNESS MIRRORS

Witness mirrors are used to measure the optical effects of NVR. These mirrors are placed on or near the optical systems of interest during test and development phases so that they are exposed to the same environmental contaminant conditions. Reflectance measurements are made before and after such exposure, and changes in reflectance are used to estimate the effect of the NVR on instrument function. Originally, these types of measurements were made over the same wavelength region as the instrument in question. Later, however, with the realization that almost all types of NVR are strongly absorbing at Lyman Alpha wavelength (121.6 nm) and with the development of practical means of reliably making these measurements, the method became widely used for determining the presence or absence of NVR regardless of the reason for needing this information. More recently, a trend toward measuring at least two wavelengths (e.g., 121.6 nm and 160.8 nm) has been seen. Measurement at two wavelengths decreases the possibility that a contaminant may go undetected because of an unlikely lack of sensitivity at 121.6 nm. The procedure for witness mirrors involves accurate measurement of reflectance before and after exposure and noncontaminating handling practices in between. Mirrors should be handled with clean forceps or noncontaminating gloves, by the edges, and shipped in special containers to preclude inadvertent contamination of mirror surfaces. If measurements show a large change in reflectance, indicating significant contamination, identification of that contaminant may become important. In this case, the same mirror can then be treated as a witness plate and the NVR analyzed accordingly.

WITNESS PLATES

Witness plates are used to collect NVR representative of what might be found on a sensitive test item. They usually consist of either mirrors or glass or metal plates and, like witness mirrors, are strategically placed on or near instruments in clean rooms or in test environments so that they accumulate the same NVR as the instrument. The plates may be used to determine both the amount and identification of the NVR. With good controls, this technique can be one of the most sensitive methods for quantification and identification of contaminants. The ultimate limit of detection by this method may be between 1 and 2 nm in thickness of NVR. However, there are some serious reservations about the physical meaning of such results and of implications about "molecular layers," film thickness, density, uniformity, and actual surface definition. In spite of these theoretical and philosophical questions and the validity of certain assumptions, usable and significant information can be obtained if a number of essential elements are included in the experimental technique.

The first step in analysis of NVR from a plate is to remove and concentrate the residue. Removal is generally accomplished by rinsing with an appropriate solvent such as alcohol, chloroform, 1,1,1-trichloroethane, or trichlorotrifluoroethane (Freon 113). Gentle evaporation of the solvent leaves the concentrated residue for analysis. The NVR that is finally analyzed includes only that material which was removed from the surface, and no implication can be made about what might be left. In addition, if the witness surface is different in nature from that of the test item (different material, treatment, or history), there may be different physical or chemical interactions with environmental sources of NVR, affecting the amount of material attracted to or retained on the surface.

Control of this analytical technique must be established by first verifying the suitability of the solvent. This must be done experimentally for each container, even when the best grades of solvent are chosen (spectroanalyzed, pesticide grade, etc.). The technique is straightforward and easy. A suitable evaporating dish (porcelain) is carefully weighed using an analytical balance that reads to 0.1 mg and filled with a known amount of solvent (50 to 75 ml). The solvent is removed gently on a warm steam bath (below its boiling point). In order to qualify for use in these analytical procedures, the amount of residue should be below the threshold for this balance, 0.1 mg (after equilibration of the evaporating dish with the surroundings), and infrared analysis (as discussed below) should show no measurable infrared absorption bands. Suitable solvents normally leave no visible residue in the evaporating dish.

After verifying the solvent, the experimental procedure to be followed must be selected. This decision is usually determined by both the type of result desired and the type of witness plate that was used. In any case, experimental blanks must be run on the entire procedure from washing a clean plate through an entire analysis. The chosen analysis may be quantitative, qualitative, or both.

If only the amount of NVR is to be determined, washing a 929 cm^2 (1 ft^2) witness plate and weighing the resulting residue to 0.1 mg gives a theoretical limit of detectability of 1.1 nm average thickness of residue. The primary assumptions for this calculation are uniformity of film, complete removal of NVR, density of NVR equal to unity (1 g/cm^3), ability to weight 0.1 mg, and zero background contribution from solvent and dish.

$$\begin{aligned} 0.1 \text{ mg}/929 \text{ cm}^2 (\text{1 ft}^2) &\times (1.1 \times 10^{-3}) \text{ } 929 \text{ cm}^2 (\text{1 ft}^2)/\text{cm}^2 \\ &\times 1 \text{ cm}^3/\text{g} \times 10^{-3} \text{ g/mg} \times 10^7 \text{ nm/cm} = 1.1 \text{ nm} \end{aligned}$$

Most of these assumptions are open to debate, but a reasonable limit of detection, in the practical sense, might be 10 nm of residue, with anything better requiring experimental confirmation. Smaller witness plates result in proportionately higher limits of detection. For instance, a 25.8 cm^2 (4 in^2) plate has an area of 1/36 of the large plate mentioned above and a consequent 36 times greater thickness required for detectability ($1.1 \times 36 = 39.6 \text{ nm}$ if all of the assumptions were valid).

WIPE SAMPLES

In many cases, such as when witness plates have not been used, NVR may be sampled directly, using controlled wipe sampling techniques. This method is applicable only when there is sufficient surface available for wiping (generally greater than 100 cm^2) and the surface is inert to the solvent. The sensitivity attainable with this technique is considerably less than that which can be achieved with witness plates primarily because of successive losses incurred with each additional transfer operation. Again, stringent control of each phase of the process must be demonstrated, and controls must be run with each set of samples. Solvent purity should be verified in the same manner as with witness plates. In addition, the cotton-tipped swabs used for sampling must receive extensive pretreatment to guarantee their cleanliness before use. This cleanup can best be accomplished by Soxhlet extraction of the swabs including, as a final step, a sufficient number of cycles using the solvent of choice so that subsequent chemical analysis of the cleaned swabs shows no detectable residue. The sampling technique itself is fairly straightforward and involves wiping the area of test surface with a solvent dampened swab, slowly rotating the swab with each stroke to present clean parts of the swab. The wipe sample can then be placed in a clean glass container (e.g., a cleaned, glass-stoppered test tube) and sent to the laboratory for analysis. This analysis begins by extraction of the sample from the swab by warming it in a small beaker with the chosen solvent for 20 to 30 minutes followed by squeezing and rinsing with fresh clean solvent. Careful evaporation of the solvent then leaves the NVR in the bottom of the beaker for chemical analysis.

DIRECT EXTRACTION

Another useful sampling method, which may be used in special cases, involves direct application of solvent to the surface and retrieval using a microsyringe. This technique may be required when witness plates are not available and wipe sampling is impractical because of restricted geometric considerations, surface roughness, or localization of suspected NVR. Preliminary requirements are verification of solvent and demonstration of cleanliness of the microsyringe. Transfer losses are minimized with this procedure since the only transfers are from surface to syringe and from syringe to potassium bromide crystal for infrared analysis. However, because of the restricted area that can be sampled by this method, the estimated sensitivity is about equivalent to that of wipe sampling. Sometimes, when higher sensitivity is required and no other method is applicable, larger areas of flight hardware can be sampled by solvent rinsing and collecting the rinse solvent for analysis. This method is usually limited by geometric considerations and proximity of solvent-sensitive materials. However, when it is properly used, it becomes equivalent to using a witness plate with the hardware surface acting in that capacity.

CHEMICAL ANALYSIS

Chemical identification of NVR is usually accomplished using infrared spectrophotometry, mass spectrometry, or both. Infrared spectra are molecular "fingerprints" having absorption bands corresponding to the frequencies of the intramolecular vibrations characteristic of the functional groups within the molecule. An infrared analysis requires passage of the infrared beam through the sample and into a grating spectrophotometer, or an interferometer-type spectrophotometer. Fortunately, the properties of NVR (i.e., nonvolatile at ambient conditions and general solubility in organic solvents) allow implementation of a sensitive, straightforward, and rapid sample preparation procedure called "casting a film." This technique involves dissolution of the sample in a few drops of solvent, transfer to a potassium bromide crystal (transparent to infrared), and evaporation of the solvent to leave only the residue film. The technique has the advantage of excellent sensitivity with the limit of detectability being near 1 microgram and is a nondestructive test. Reliable interpretation of the resulting spectra requires the services of an experienced analytical chemist. Some examples of the spectra of common constituents found in studies of aerospace NVR can be found in NASA Technical Note, NASA TN D-8451. Most often, NVR consists of mixtures of compounds, and the analysis by infrared provides only the classes of those chemical species present.

In addition to identification, infrared curves may also be used to provide quantitative estimates of the amounts of NVR present. This requires considerable skill and preparation of extensive calibration curves but has the advantage of requiring a much smaller sample than can readily be weighed on a standard analytical balance. Thus, the thickness of NVR that is measurable on the small mirror considered previously (25.8 cm^2) becomes comparable to weighing the sample from the 929 cm^2 (1 ft^2) plate.

When the results of the infrared analysis are insufficient and more specific information is desired, the sample may be subjected to various types of mass spectral analysis. Again, this technique requires the services of an experienced mass spectrometrist and also requires more expensive and sophisticated instrumentation. However, the results are often spectacular and provide previously unattainable insights into the nature of the NVR, including probable sources and possible consequences of the presence of these contaminants. They may provide separation of complex mixtures, exact molecular identification of components, and profiles of the volatility characteristics of the NVR. The sensitivity of these methods is at least ten times better than with infrared, and in certain cases, two or three orders of magnitude may be achieved. To make use of this added sensitivity, it is necessary to run additional blank control samples to ensure the credibility of the results. The same sample used for the infrared analysis may be transferred to the mass spectrometer by dissolving it in a solvent and either depositing it on the direct probe or injecting it into the gas chromatograph inlet. Although the details of mass spectrometric analysis are beyond the scope of this report, the basic operating principle of the mass spectrometer involves energetic ionization of the sample, recording of the positive ion fragmentation patterns and intensities (unique for each molecular structure), and computer-assisted data handling and comparison of results with extensive data banks or libraries. Examples of mass spectral data for NVR materials are included in NASA Technical Note, NASA TN D-8261.

SUMMARY

Because the presence of small amounts of organic contaminants on various spacecraft surfaces can have severe effects on the successful operation of many advanced scientific experiments, the detection and identification of such contaminants are often essential. There are four practical methods for determining the presence of such contaminants (NVR) and collecting samples for analysis. These methods include the use of witness mirrors, witness plates, wipe sampling, and direct solvent extraction. Each method requires the implementation of controlled analytical techniques and materials, and control samples are always essential. Solvents and wiping materials must be shown to contribute no detectable residue to the NVR sample. The development of a "standard method" for analysis of NVR on spacecraft hardware appears to be impractical because of the complexity and uniqueness of each real-life situation. Differences in physical and chemical makeup of structures, as well as differences in intent of analysis, always require the presence of experienced, decision-making professionals to elicit the appropriate response to a need for analysis of NVR.